

TRACE ELEMENT CONCENTRATIONS IN PYRRHOTITES FROM ORGUEIL (CI).

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In many chondritic meteorites the host phases of trace elements such as copper, zinc, germanium, and selenium are not well known. Therefore, we analyzed 20 hand-picked pyrrhotite (Fe_{1-x}S) grains from Orgueil (CI) by Analytical Scanning Electron Microscopy and Synchrotron X-Ray Fluorescence Microprobe for major, minor and trace elements. Our results suggest that pyrrhotite is not the main host phase of Cu, Zn, and Ge in Orgueil. In most grains the concentrations of these elements are below CI. Surprisingly, the selenium concentrations are also not high enough to qualify pyrrhotite as the main selenium-bearing phase. This is in sharp contrast to all previous assumptions and requires intensive search for the real host minerals of this important chalcophile element.

INTRODUCTION. In most chondritic meteorites copper, zinc, germanium, and selenium are minor elements having concentrations of ~10-500 ppm (Cu), ~35-700 ppm (Zn), ~7-40 ppm (Ge), and ~2-21 ppm (Se) depending on the meteorite class studied [1-4]. Trace element analyses have shown that copper and germanium are concentrated in the phases like taenite and kamacite [1, 3]. In contrast, silicates and oxides, e.g. chromite (FeCr_2O_4), have been identified as the main zinc-bearing phases [1, 2]. Dreibus et al. [4] suggested that selenium, the only truly chalcophile element in chondritic meteorites, is completely hosted in sulfides like pyrrhotite (Fe_{1-x}S), troilite (FeS), pentlandite ($(\text{Fe,Ni})_9\text{S}_8$), and cubanite (CuFe_2S_3) [1, 4]. However, only very few data are available for the abundances of these important elements in certain phases from carbonaceous chondrites. Pyrrhotites are the most abundant sulfides in CI meteorites [e.g. 5]. Therefore, we performed trace element analyses of selected pyrrhotites from the Orgueil (CI) meteorite.

EXPERIMENTAL. For the separation of the pyrrhotite grains, a 2 mm fragment of Orgueil (CI) was crushed between two glass plates. After washing with ethanol 20 euhedral pyrrhotite grains were hand-picked from the fine-grained residue (Fig. 1). The individual particles were then analyzed by Analytical Scanning Electron Microscopy (Institute of Planetology) and Synchrotron X-Ray Fluorescence Microprobe (National Synchrotron Light Source at Brookhaven National Laboratory) for major, minor and trace elements.

RESULTS. Most pyrrhotite grains show a great variety in major as well as in trace element concentrations (Table 1). The iron content ranges from 43.6 to 55.7 wt%, sulphur from 42.7 to 55.3 wt% and nickel from 0.94 to 1.74 wt%. The factor $1-x$, in Fe_{1-x}S , indicating iron vacancies in the pyrrhotite structure, is between 0.65 and 0.81. In nearly all pyrrhotites the concentration of copper is low (20-80 ppm) compared to the CI value of 119 ppm [6]. However, some grains show almost CI abundances (P1, P16 and P20) and two sulfides are strongly enriched (P6 and P11). Zinc is also low in most of the pyrrhotites relative to CI (312 ppm, [6]). Whereas in four grains the Zn concentration is below the detection limit (~5 ppm), the majority of the sulfides have zinc between 9 and 50 ppm. Zinc values of 96-181 ppm have been detected in three grains but this is still far below the CI value. With the exception of one pyrrhotite grain (P10), the germanium concentrations are below the detection limit of ~5 ppm. Even in case of P10 only 9 ppm Ge were measured (CI: 32.6 ppm; [6]). All pyrrhotites contain considerable amounts of selenium. The concentrations are in the range of 36-100 ppm, all well above the CI value of 18.2 ppm [5].

DISCUSSION. Our data confirm in general the assumption that pyrrhotite is not the main host phase of copper, zinc and germanium in CI meteorites. Only very few grains contained these elements in concentrations high enough to contribute significantly to the CI values. In contrast, the statement made by Dreibus et al. [4] that sulfides are the main selenium-bearing phase seems to be incorrect in case of Orgueil. Pyrrhotites are the most abundant sulfides in Orgueil. Assuming them as the main Se-hosting phase they should contain, with respect to their sulphur content, approximately 145-182 ppm Se (8-10 x CI). However, only between 36 and 100 ppm (2-5 x CI) have been found. Consequently, there must be other mineral phases containing significant amounts of selenium in Orgueil. Possible candidates are other sulfides like pentlandite and cubanite but, since these sulfides are less abundant than pyrrhotite they would have to contain much higher selenium concentrations, probably in the range of about 1000 ppm or more. Also the phyllosilicates in which Se might be more or less homogeneously distributed may be main host phases of Se. Further studies are needed to answer these questions.

References: [1] Mason B. and Graham A. L. (1970) *SCES* 3. [2] Nishimura M. and Sandell E. B. (1964) *GCA* 28, 1055. [3] Bernstein L. R. (1985) *GCA* 49, 2409. [4] Dreibus G. et al. (1995) *Meteoritics* 30, 439. [5] Kerridge J. F. et al. (1979) *EPSL* 43, 359. [6] Anders E. and Grevesse N. (1989) *GCA* 53, 197.

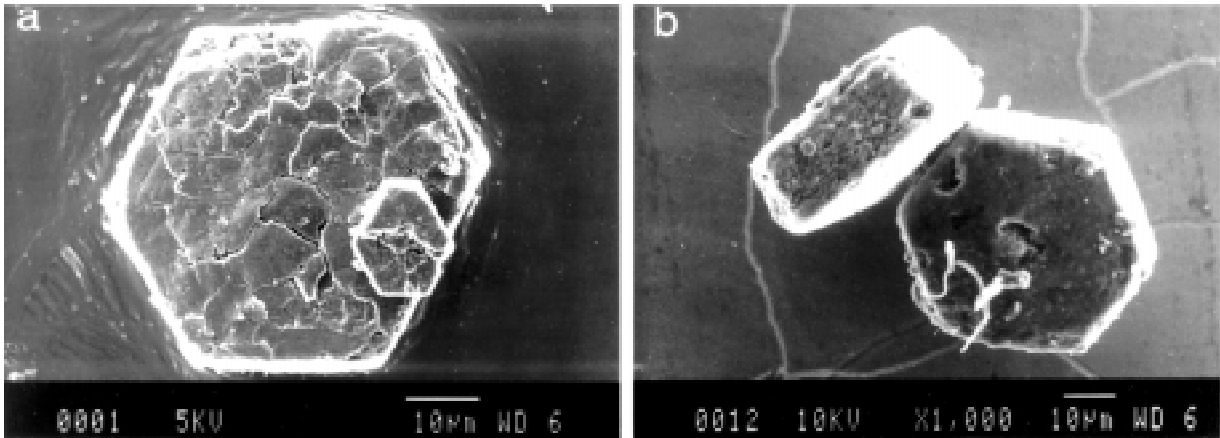


Fig.1 SE-images of selected pyrrhotite grains from Orgueil (CI).

Table 1. Chemical composition of pyrrhotites from Orgueil (CI). Major elements analyzed by ASEM (*, EDX, wt%); trace elements analyzed by SXRF (ppm); b.d.: below detection limit.

| | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | P9 | P10 |
|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|-------|
| | % | % | % | % | % | % | % | % | % | % |
| Fe* | 43.6 | 51.0 | 49.5 | 46.7 | 52.0 | 55.7 | 53.7 | 46.0 | 50.7 | 47.5 |
| S* | 55.3 | 47.8 | 48.8 | 51.8 | 46.5 | 42.7 | 44.7 | 53.0 | 47.7 | 51.3 |
| Ni* | 1.02 | 1.12 | 1.67 | 1.48 | 1.44 | 1.56 | 1.65 | 1.06 | 1.67 | 1.14 |
| Total | 99.92 | 99.92 | 99.97 | 99.98 | 99.94 | 99.96 | 100.05 | 100.06 | 100.07 | 99.94 |
| 1-x | 0.65 | 0.77 | 0.74 | 0.70 | 0.78 | 0.93 | 0.81 | 0.69 | 0.76 | 0.71 |
| | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Cu | 110 | 20 | 30 | 70 | 40 | 340 | 50 | 40 | 40 | 50 |
| Zn | b.d. | 18 | 36 | 13 | b.d. | 154 | b.d. | 20 | 26 | 10 |
| Ge | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. |
| Se | 51 | 63 | 71 | 52 | 63 | 97 | 78 | 61 | 50 | 51 |

| | P11 | P12 | P13 | P14 | P15 | P16 | P17 | P18 | P19 | P20 |
|-------|--------|--------|--------|--------|--------|-------|--------|-------|-------|--------|
| | % | % | % | % | % | % | % | % | % | % |
| Fe* | 54.3 | 51.7 | 47.8 | 48.5 | 51.8 | 49.6 | 49.0 | 53.2 | 50.7 | 52.0 |
| S* | 44.0 | 47.1 | 51.2 | 50.3 | 46.6 | 49.1 | 49.7 | 45.3 | 47.6 | 46.3 |
| Ni* | 1.74 | 1.22 | 0.94 | 1.24 | 1.64 | 1.28 | 1.37 | 1.47 | 1.69 | 1.73 |
| Total | 100.04 | 100.02 | 100.09 | 100.04 | 100.04 | 99.98 | 100.07 | 99.97 | 99.99 | 100.03 |
| 1-x | 0.81 | 0.77 | 0.71 | 0.72 | 0.78 | 0.74 | 0.73 | 0.79 | 0.76 | 0.78 |
| | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Cu | 310 | 60 | b.d. | 40 | 40 | 100 | 70 | 70 | 80 | 150 |
| Zn | 22 | 181 | 50 | b.d. | 45 | 19 | 9 | b.d. | 11 | 96 |
| Ge | 9 | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. |
| Se | 81 | 81 | 100 | 53 | 57 | 67 | 71 | 36 | 54 | 56 |